Synthesis and Properties of Dioxa[3.3](3,6)carbazolophane

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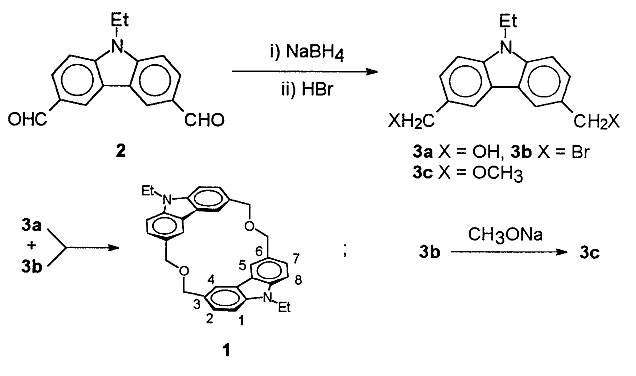
(Received October 30, 1995)

Dioxa[3.3](3,6)carbazolophane **1** has been synthesized by the cyclization reaction between 3,6-bis(hydroxymethyl)carbazole and corresponding dibromide. The transannular π-π electronic properties of **1** in solution were examined by absorption and emission spectra. The structure of **1** was confirmed by X-ray crystal analysis.

Poly(*N*-vinyl carbazole) is a well-known photoconductor and photophysical processes of the carbazole chromophore have been the center of much attention from the fundamental as well as the application standpoint.[1] Many workers have investigated the electronically excited states and their relaxation processes in the polymer and its dimer model compounds.[2,3] For the excimer of carbazole chromophore in the excited singlet state, the structural requirement has been extensively studied and the sandwich and partial-overlap excimers were established. However, the geometrical structure of triplet excimer has not been clarified yet, because it is very difficult to observe phosphorescence in liquid solutions. For the triplet excimer, the cyclophane is a candidate to elucidate the structural geometry. Cyclophanes have been used to study the transannular π-π electronic interaction and charge transfer interaction in various aromatic systems.[4] Many condensed benzenoid cyclophanes such as naphthalenophanes, anthracenophanes and pyrenophanes were synthesized and their excited state interaction as well as the transannular interaction has been extensively examined.[4,5] Although rigidly fixed carbazolophane (cyclophane which contains carbazole) is suitable for studying the excited state interaction between carbazole chromophores, this cyclophane has not been reported yet. Herein, we report the synthesis of dioxa[3.3](3,6)carbazolophane **1** and its chemical and spectral properties.



Treatment of 9-ethylcarbazole with an excess of phosphoryl chloride and *N*,*N*-dimethylformamide in dibromomethane at reflux for 30 h afforded the 3,6-bis(formyl)-9-ethylcarbazole **2**[6] in 51% yield together with the mono-formylated product. Reduction of **2** with sodium borohydride in ethanol, followed by hydrolysis with sat. aq. sodium hydrogencarbonate gave 9-ethyl-3,6-bis(hydroxymethyl)carbazole **3a**[7] in 83% yield. Attempts at converting the hydroxyl group in **3a** by acid halides into corresponding halides were all unsuccessful, only giving dark blue polymeric material. On the other hand, an excess of concd. hydrobromic acid was added to a suspension of **3a** in chloroform at 0 °C to give the desired dibromide **3b**[8] in 80% yield, which was easy to decompose. The cyclization reaction between **3a** and **3b** was allowed to proceed in the presence of sodium hydride in tetrahydrofuran at reflux under Ar atmosphere using high dilution technique. The reaction mixture was purified by alumina chromatography and recrystallization to give **1**[9] in 35% yield. Methoxy derivative **3c**[10] was also prepared as a reference. The chemical shifts for aromatic protons of **1** and **3c** appeared as a typical ABX system. Almost all protons of **1** except H_4 protons shifted to the low-field due to the anisotropic effect from the opposite aromatic ring by ca. 0.09 ppm compared with those of **3c**. This indicated that the stacking mode of two carbazole rings in **1** was of anti-conformation, which might lead to small overlap between carbazole rings.

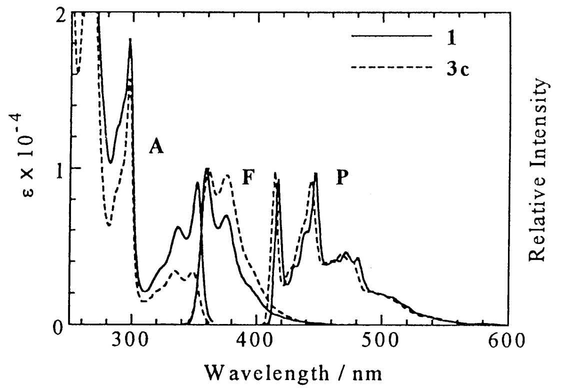


Figure 1. Absorption spectra in tetrahydrofuran (**A**) and fluorescence (**F**) and phosphorescence (**P**) spectra of **1** and **3c** in 2-methyltetrahydrofuran. Emission spectra are normalized at the maximum of each spectrum peak.

Figure 1 shows the spectral data of **1** and **3c**. The absorption and fluorescence spectra were obtained at 20 °C and the phosphorescence measurements were carried out at the liquid nitrogen temperature, 77 K. The main absorption bands in **1** showed only a small bathochromic shift from **3c**, reflecting the anti-conformation in **1**. The absorption band around 350 nm maxima of **1** showed a hyperchromic effect, which suggests the existence of the transannular π-π electronic interaction. Electronic properties of the present system in solution were further correlated with their crystal structure as given in Figure 2. X-ray crystal analysis of **1** revealed that the carbazole rings were connected closely by two bridges (the intramolecular nonbonded distance between the facing carbazole rings; 3.23 Å) though they did not face each other. The transition moments corresponding to the absorption around 350 nm direct toward the short axis of the carbazole ring.[11] When the carbazole rings are in anti-conformation, the transition moments arrange almost head-to-tail. From this arrangement, the small bathochromic shift of **1** is explained.

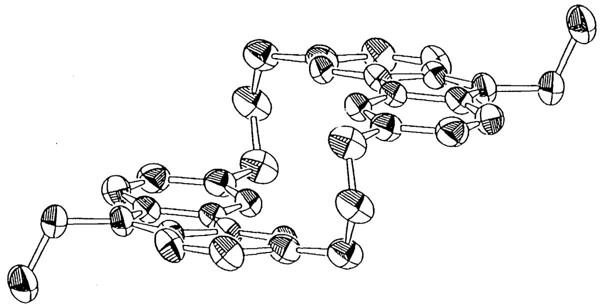


Figure 2. A perspective view of carbazole cyclophane **1**.

The fluorescence spectrum of **1** is a mirror image of the absorption spectrum and no excimer emission was observed around 445 nm. This indicates that **1** does not isomerize to the syn-form at 20 °C in 2-methyltetrahydrofuran solution. The phosphorescence spectrum of **1** red-shifted as compared with that of **3c**, but no excimer phosphorescence appeared. In our previous work,[12] we reported that the triplet excimer was formed in poly[2-(9-carbazolyl)ethyl methacrylate] film. In this polymer, the pendant chromophore is linked to the main chain with a few spacer atom and is free from steric restriction intramolecularly imposed by the so-called *n = 3 rule*,[13] which usually results in efficient excimer formation in vinyl polymers.[14] These indicate that the triplet excimer is formed intermolecularly and its potential energy curve is probably loose with respect to the arrangement of chromophores. Carbazole chromophores in **1** are sufficiently close but the triplet excimer did not form. This indicates that the triplet excimer needs more geometrical requirements such as more π-electron overlap besides the closeness of the chromophores. To study the structure of the triplet excimer of carbazole in detail, synthesis of [2.2] and [3.3] carbazolophanes is now in progress.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, Photochemical Reactions (No. 06239107) from the Ministry of Education, Science, Sports and Culture of Japan.

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6 **2**: mp 173-174 °C, colorless needles (benzene): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.52 (3H, t, J = 7.3 Hz), 4.47 (2H, q, J = 7.3 Hz), 7.57 (2H, d, J = 8.6 Hz), 8.10 (2H, dd, J = 8.6 Hz, 1.7 Hz), 8.68 (2H, d, J = 1.7 Hz), 10.14 (2H, s): Found: C, 76.09; H, 5.07; N, 5.54%. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%.

7 **3a**: mp 163-165 °C, colorless needles (EtOH): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.43 (3H, t, J = 7.3 Hz), 1.64 (2H, t, J = 5.3 Hz), 4.38 (2H, q, J = 7.3 Hz), 4.86 (4H, d, J = 5.3 Hz), 7.41 (2H, d, J = 8.3 Hz), 7.51 (2H, dd, J = 8.3 Hz, 1.7 Hz), 8.10 (2H, d, J = 1.7 Hz): Found: C, 75.22; H, 6.61; N, 5.39%. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%.

8 **3b**: mp 158-159 °C, colorless needles (benzene-hexane): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.41 (3H, t, J = 7.3 Hz), 4.33 (2H, q, J = 7.3 Hz), 4.77 (4H, s), 7.36 (2H, d, J = 8.6 Hz), 7.51 (2H, dd, J = 8.6 Hz, 1.7 Hz), 8.10 (2H, d, J = 1.7 Hz): Found: C, 50.16; H, 4.01; N, 3.62; Br, 42.00%. Calcd for $C_{16}H_{15}NBr_2$: C, 50.42; H, 3.97; N, 3.68; Br, 41.93%.

9 **1**: dec > 295 °C, colorless needles (chloroform-hexane): ^{1}H NMR ($CDCl_3$, 270 MHz) δ1.50 (6H, t, J = 7.3 Hz), 4.43 (4H, q, J = 7.3 Hz), 4.71 (8H, s), 7.46 (4H, d, J = 8.2 Hz), 7.53 (4H, dd, J= 8.2 Hz, 1.7 Hz), 8.08 (4H, d, J = 1.7 Hz): Found: C, 81.10; H, 6.10; N, 5.84%. Calcd for $C_{32}H_{30}N_2O_2$: C, 80.98; H, 6.37 ; N, 5.90%.
Crystal data for compound **1**: $C_{32}H_{30}N_2O_2$ Molecular weight 474.6, monoclinic system space group $P2_1/c$, Z = 2, a = 10.736(1), b = 5.820(2), c = 19.083(3)Å, β = 89.99(1)°, V = 1192.5(5)$Å^3$. Dc = 1.32 g cm^{-3}. Intensity data were collected by the ω-2θ scan mode on a Rigaku AFC7R diffractometer using Mo-Kα radiation. The structures were solved by direct methods (SAPI91) and refined by full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically. The final refinement converged with R = 0.044 and R_w = 0.045 (function minimized $\Sigma w(|Fo|-|Fc|)^2$, w = $1/\sigma^2(Fo)$) for 754 [I > 3.0σ(I)] reflections.

10 **3c**: mp 49-50 °C, colorless needles (EtOH): ^{1}H NMR ($CDCl_3$, 270 MHz) δ1.40 (3H, t, J = 7.3 Hz), 3.41 (6H, s), 4.34 (2H, q, J = 7.3 Hz), 4.63 (4H, s), 7.37 (2H, d, J = 8.3 Hz), 7.45 (2H, dd, J= 8.3 Hz, 1.7 Hz), 8.07 (2H, d, J = 1.7 Hz): Found: C, 76.27; H, 7.53; N, 4.88%. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94%.

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